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## NLO properties of $\text{Si}(\text{OH})_4$ and $\text{Ge}(\text{OH})_4$ clusters

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### Abstract

The NLO properties in terms of static and frequency-dependent hyperpolarizabilities of  $\text{Si}(\text{OH})_4$  and  $\text{Ge}(\text{OH})_4$  clusters are determined with an aim to understand the microscopic NLO behavior of silica. The calculated results reveal that the cluster configuration induced by the presence of a defect plays a significant role in determining the non-linear response of these clusters. In addition, instant ionization of the cluster introduces a noticeable increase in the value of second hyperpolarizability,  $\gamma$ .

Nonlinear optics is currently at the forefront of research because it is the key technology for optical communication, signal processing and computing [1]. Photonic switches made out of nonlinear optical (NLO) materials have potential advantages of wide-band frequency domain, immunity to electromagnetic induction, and high-speed operation over electrical switches. Glassy materials are one of the prime candidates for photonic switches due to their ease of fabrication, high transparency and high chemical and thermal stability [2].

Nonlinear optical properties of glasses are known to be correlated with the third-order susceptibility due to the absence of ordered dipoles. However, Kester et al. [3] have observed frequency doubling in Ge-doped silica suggesting that even glasses have frequency doubling capability. Similar observations have been made in bulk and thin films of silica grown on semiconductor substrates [4].

The present work attempts to provide a basis to understand the origin of such NLO effects in pure and impurity-doped silica at the molecular level. Our efforts will be directed to hyperpolarizability calculations of the molecular units, namely  $\text{Si}(\text{OH})_4$  and

$\text{Ge}(\text{OH})_4$  clusters (Fig. 1) in the Hartree-Fock framework. Each oxygen atom at the cluster boundary is attached by a hydrogen atom in such a way that they simulate O-Si bond directions. The optimum configurations of these nine-atom clusters are obtained using a general atomic and molecular electronic structure program [5], GAMESS.

The NLO properties have been shown to be very sensitive to the choice of basis set. For the case of

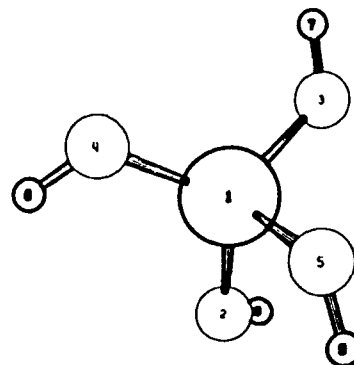


Fig. 1. Geometrical configuration of the  $\text{X}(\text{OH})_4$  cluster where X is Si or Ge.

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ethylene, a sufficiently flexible valence Gaussian basis set, such as a 3-21G or 6-31G, augmented by diffuse p and d functions on C atoms is found to be necessary for a satisfactory description of various tensor components of the static polarizability and second hyperpolarizability [6]. For  $\text{Si}(\text{OH})_4$  and  $\text{Ge}(\text{OH})_4$  clusters, we use double-zeta valence (dzv) basis sets, with a diffuse d polarization function to describe cluster atoms. The basis set consists of 6s and 4p and 1d Gaussian functions for Si [7], 6s, 4p and 2d for Ge [8], 3s, 2p and 1d for C [7] and 2s for H [7].

For the dipole moment of a molecule interacting with a static electric field ( $F$ ), we can write

$$\mu_i = \mu_{i0} + \alpha_{ij} F_j + \frac{1}{2} \beta_{ijk} F_j F_k + \frac{1}{6} \gamma_{ijkl} F_j F_k F_l + \dots \quad (1)$$

where  $\mu_{i0}$  is the permanent dipole moment and  $\alpha_{ij}$ ,  $\beta_{ijk}$  and  $\gamma_{ijkl}$  are tensor elements of the linear polarizability, and first and second hyperpolarizabilities, respectively, of the molecule [9]. Likewise, one can write an expression for dynamic fields relating  $\beta$  and  $\gamma$  to experiments such as second harmonic generation, optical rectification, and Kerr effect [10]. In Eq. (1), the subscripts  $i, j, k$ , and  $l$  represent Cartesian axes and the summation of repeated indices is assumed.

First, we obtain the potential energy surfaces of both neutral (geom A,  $q=0$ ) and ionized states (geom B,  $q=+1$ ) of the  $\text{X}(\text{OH})_4$  cluster (X being Si

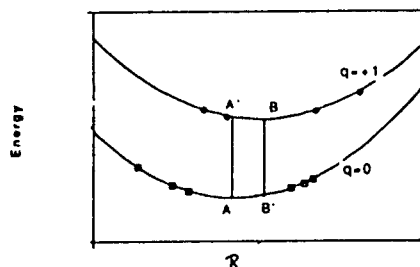


Fig. 2. Sketch of the potential energy surface of the neutral and ionized  $\text{X}(\text{OH})_4$  cluster where X is Si or Ge.

or Ge) and then calculate their hyperpolarizabilities at the optimum configuration. The  $q=+1$  charge state is expected to mimic the defect-induced effect on the NLO properties. We also use the vertical approximation for calculations of the single point A' (geom A,  $q=+1$ ) and B' (geom B,  $q=0$ ) as shown in Fig. 2.

Table 1 shows the geometric parameters, namely the bond length and the bond angles of the optimized configuration obtained with dzv and dzvP (including polarization function, d) basis sets. The results obtained using both the basis sets show similar trends. For example, the substitution of Ge for Si increases the bond length. Mulliken population analysis predicts Ge to be less electronegative than Si. For the ionized cluster ( $q=+1$ ), the optimized configuration shows the hole localizing on one of the neighboring oxygens resulting in an increase of its bond length.

Table 1

Total energy and configurational parameters of neutral and ionized  $\text{Si}(\text{OH})_4$  and  $\text{Ge}(\text{OH})_4$  clusters

		$R(\text{X}-\text{O}(i), i=2, 5)$ (Å)	$\angle(\text{O}(2)-\text{X}-\text{O}(i), i=3, 5)$ (deg)	Total energy (hartree)
<b>Si(OH)<sub>4</sub></b>				
$q=0$	dzv	1.652, 1.652, 1.652, 1.652	107.3, 113.8, 107.3	-590.8126
	dzvP	1.628, 1.628, 1.628, 1.628	106.5, 115.7, 106.5	-590.9846
	6-31G [11]	1.665, 1.665, 1.673, 1.673	115.5, 107.8, 106.2	-590.7039
$q=+1$	dzv	1.594, 1.600, 1.584, 1.943	117.8, 119.4, 95.6	-590.4592
	dzvP	1.578, 1.582, 1.575, 1.900	118.2, 119.8, 95.0	-590.5971
	6-31G [11]	1.602, 1.918, 1.615, 1.608	102.8, 116.9, 120.2	-590.3531
<b>Ge(OH)<sub>4</sub></b>				
$q=0$	dzv	1.726, 1.726, 1.726, 1.726	107.6, 113.3, 107.6	-2375.0059
	dzvP	1.734, 1.734, 1.734, 1.734	106.3, 115.9, 106.3	-2375.3107
$q=+1$	dzv	1.655, 1.653, 1.654, 1.953	117.7, 118.6, 96.4	-2374.6614
	dzvP	1.694, 1.691, 1.692, 1.999	116.1, 116.1, 91.6	-2374.9574

For comparison, we include the results of Rao et al. [11] using the 6-31G basis set for the  $\text{Si}(\text{OH})_4$  clusters in Table 1.

In order to judge the character of predicted configuration on the potential energy hypersurface, we calculated the frequency of the neutral  $\text{Si}(\text{OH})_4$  cluster (i.e. geom A) in the harmonic approximation. The calculated frequencies in the rocking, bending and stretching modes come out to be 465, 828 and 1041  $\text{cm}^{-1}$ , showing a good agreement with the corresponding experimental values [12] of 450, 812 and 1058  $\text{cm}^{-1}$ , respectively.

Table 2 lists dipole moment and the hyperpolarizabilities for the  $\text{Si}(\text{OH})_4$  and  $\text{Ge}(\text{OH})_4$  clusters. As we ionize the cluster (freezing the configuration at  $q=0$ ), the  $\beta$  and  $\gamma$  show a large, noticeable increase. The optimized configuration (for  $q=+1$ ) retains the somewhat larger  $\beta$  value. However, when we make the cluster charge neutral, both the dipole moment and  $\beta$  show an increase in their values. Similar observations have been made for the  $\text{Ge}(\text{OH})_4$  cluster. Note that for  $q=+1$  (at  $q=0$  configuration) a large increase of  $\gamma$  is predicted.

The results therefore reveal that the cluster configuration plays a key role in predicting a large  $\beta$  value related to second-harmonic generation or Kerr effect. A dependence of  $\beta$  on the cluster dipole moment resulting from the distorted configuration is also shown here. On the other hand, instant ionization of the cluster leads to a significant increase in  $\gamma$  that is related to DC-SHG and THG experiments.

Table 2  
Dipole moment and polarizabilities (in atomic units) of neutral and ionized  $\text{Si}(\text{OH})_4$  and  $\text{Ge}(\text{OH})_4$  clusters at different geometries shown in Fig. 2

	Dipole moment	$\beta$	$\gamma$
<b><math>\text{Si}(\text{OH})_4</math></b>			
geom A ( $q=0$ )	0.00	0.00	945.8
A' ( $q=+1$ )	0.00	5.84	22420.8
B ( $q=+1$ , opt)	0.24	31.81	3008.9
B' ( $q=0$ )	1.67	63.6	1455.1
<b><math>\text{Ge}(\text{OH})_4</math></b>			
geom A ( $q=0$ )	0.00	0.23	1248.1
A' ( $q=+1$ )	0.00	34.5	66066.5
B ( $q=+1$ , opt)	0.59	1.42	1690.9
B' ( $q=0$ )	1.36	90.0	2226.3

Table 3

Time-dependent Hartree-Fock results for the  $\text{Si}(\text{OH})_4$  cluster at 1064 nm in atomic units

	Geom A	Geom B'
SHG	0.11	63.8
Kerr effect	0.11	61.5
DC-SHG	1185.7	1713.4
THG	1254.5	1848.7

It has been suggested that the dispersion of NLO effects is of great importance for the application of conjugated polymers to photoionic studies. But this is not found to be the case for both the  $\text{Si}(\text{OH})_4$  and  $\text{Ge}(\text{OH})_4$  clusters. We give the results of time-dependent Hartree-Fock (TDHF) calculations using the program package ACES II [13] at 1064 nm in Table 3. Although the frequency-dependent values are predicted to be about the same as the static values, they do confirm the role of configuration for a larger  $\beta$  value. Our results therefore suggest that the cluster configuration induced by the presence of a defect plays a role for the NLO effect at the molecular level in the  $\text{Si}(\text{OH})_4$  and  $\text{Ge}(\text{OH})_4$  clusters.

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## References

- [1] J.D. Mackenzie, C.Y. Li and Y. Xu, Chem. Express 6 (1991) 903.
- [2] E.J. Friebel and D.L. Griscom, Mater. Res. Symp. Proc. 61 (1986) 319.
- [3] J. Kester et al., private communication.
- [4] R.A. Myers, N. Mukherjee and S.R. Brueck, Nonlinear Optics: Topical Meeting, August 17-21, 1992, Hawaii, abstract MA3.
- [5] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, J.H. Jensen, S. Koseki, M.S. Gordon, K.A. Nguyen, T.L. Windus and S.T. Elbert, QCPE Bull. 10 (1990) 52.
- [6] S.P. Karna, G.B. Talapatra, W.M.K.P. Wijekoon and P.N. Prasad, Phys. Rev. A 45 (1992) 2763.
- [7] T.H. Dunning Jr. and P.J. Hay, in: Methods of electronic structure theory, ed. H.F. Schaefer III (Plenum Press, New York, 1977) p. 1.

- [8] R.C. Binning Jr. and L.A. Curtiss, *J. Comput. Chem.* 11 (1990) 1206.
- [9] C. Flytzanis, in: *Theory of nonlinear optical susceptibilities, quantum electronics*, eds. H. Rabin and C.L. Tang (Academic Press, New York, 1975).
- [10] D.S. Chemla and J. Zyss, eds., *Nonlinear optical properties of organic molecules and crystals*, Vols. I and II (Academic Press, New York, 1987).
- [11] P.S. Rao, R.J. McEachern and J.A. Weil, *J. Comput. Chem.* 12 (1991) 254.
- [12] H.M. Dauplaise, K. Vaccaro, B.R. Bennett and J.P. Lorenzo, *J. Electrochem. Soc.* 139 (1992) 1684.
- [13] H. Sekino and R.J. Bartlett, *J. Chem. Phys.* 85 (1986) 976; H. Sekino and R.J. Bartlett, *J. Chem. Phys.* 94 (1991) 3665; J.F. Stanton, J. Gauss, J.D. Watts, W.J. Lauderdale and R.J. Bartlett, University of Florida (1991).

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